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Journal of Magnetism and Magnetic Materials 201 (1999) 234–237

Journal of magnetism and magnetic materials

www.elsevier.com/locate/jmmm

Phase separation in magnetic colloids

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Received 4 May 1998; received in revised form 6 August 1998

Abstract

The influence of a temperature, a magnetic field strength and an excess electrolyte on the phase separation conditions in magnetic colloids has been studied theoretically, taking into account the ferroparticle polydispersity. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Phase separation; Magnetic fluids

1. Introduction

Three main reasons for the phase separation in magnetic colloids are known [1,2]: (a) decrease in temperature which leads to a violation of thermodynamic stability in a system of dispersed ferroparticles; (b) increase in the concentration of electrolyte, resulting in the formation of a rather deep secondary energy minimum due to a decrease in the thickness of the electrical double layers; (c) strengthening of an external magnetic field. This is associated with the fact that the non-central dipole–dipole interaction of the ferroparticle magnetic moments displays itself on the whole as an effective interparticle attraction. The intensity of this attraction increases in an external field, thus a magnetic field stimulates the process of phase separation in ferrocolloids. All these reasons are theoretically investigated, taking into account the ferroparticle polydispersity on the basis of thermodynamic perturbation model of magnetic colloids.

2. Thermodynamic model

Sizes of the ferroparticle magnetic cores in real magnetic fluids (MF) ($x \sim 8$–10 nm), taking into account the nonmagnetic layers on their surfaces, give typical values of the dimensionless energy of the magneto-dipole interparticle interaction of the order of $\gamma = m^2/d^3kT \sim 0.1$–$0.5$ (m – ferroparticle magnetic moment, d – diameter of a ferroparticle including the non-magnetic layers, kT – thermal energy). A potential minimum of such a depth is not sufficient for a condensation to occur. Various authors [3–5] give the values of the energy minimum required for a phase transition in the range $\gamma \sim 2$–4.5, i.e. an order larger than is realized experimentally. In addition, all existing theories are based on the assumption of monodispersity, and they are unable to explain a number of effects in

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PII: S0304-8853(99)00050-5

principle (e.g. the difference in the dispersities of weakly and strongly concentrated phases [1]). Thus, by not taking into account the polydispersity of MF, one can only assume a qualitative description of the process of phase separation.

The peculiarities brought by the polydispersity into the process of phase separation can be estimated even in an example of a two-fraction system. The real particle size distribution can be substituted by a model bidisperse distribution with the help of conditions of equality of the observed magnetostatic characteristics. The equalities of the mean magnetic moment and the mean-squared magnetic moment give the opportunity to determine the ferroparticle sizes and the molar fractions of bidisperse ferrocolloid. The results obtained are the following [6,7]: the main fraction is characterized by the magnetic core diameter $x_1 \sim 6$–8 nm and the molar portion $v_1 \sim 95\%$, the second fraction consists of a small number of large particles: $x_2 \sim 14$–17 nm, $v_2 \sim 5\%$. Due to the large difference in the magnetic core diameters, the dimensionless energy of the magneto-dipole interaction γ_{ij} between particles of different fractions varies considerably. For magnetite particles at a room temperature we obtain $\gamma_{11} \approx 0.1$–0.3, $\gamma_{22} \approx 2.5$–3. Thus, the main fraction consists of particles with negligibly weak interparticle attraction, whereas the interaction between large ferroparticles is quite intensive.

3. Influence of a temperature and a magnetic field

To analyse the conditions of equilibrium phase separation one has to require the constancy of chemical potentials of particles of both fractions in coexisting phases. This enables us to obtain the concentration and dispersity of weakly and strongly concentrated phases. Chemical potentials of ferroparticles were calculated on the basis of thermodynamic perturbation theory [5]. A decrease in temperature and a strengthening of a magnetic field result in the appearance of bends on curves of chemical potentials as functions of the concentrations of the particles of both fractions, these bends are analogous to the van der Waals loops. In these regions of concentrations, temperatures and magnetic fields, the stability of a spatially homogeneous MF state breaks down and coexisting phases originate. The point is that only the fraction of large particles (which are small in number) is thermodynamically unstable. Thus even a slight change in their number causes an essential shift in the two-phase region boundary.

The phase stability diagram in the plane T–H is demonstrated in Fig. 1 for MF with various initial concentrations of a magnetic phase. The region of higher temperatures and weaker magnetic fields corresponds to the stable homogeneous state. As Fig. 1 shows, a transfer from a monodisperse to even a model bidisperse system results in phase separation at room temperatures and weak-to-moderate magnetic fields.

Behind the phase stability boundary the MF is in the separated state. The character of the changes in the basic parameters of coexisting phases I and II can be seen in Fig. 2. Phase I occupies practically the whole system volume and consists of particles of fraction 1 with a negligibly low portion of large particles of fraction 2. The magnetic phase concentration and the mean magnetic moment of the phase I decrease monotonically with the increase of an external field or temperature lowering. Phase II contains the majority of large particles, whose concentration grows with decreasing temperature or a strengthening magnetic field. The mean magnetic moment of the phase II (droplike aggregates) is

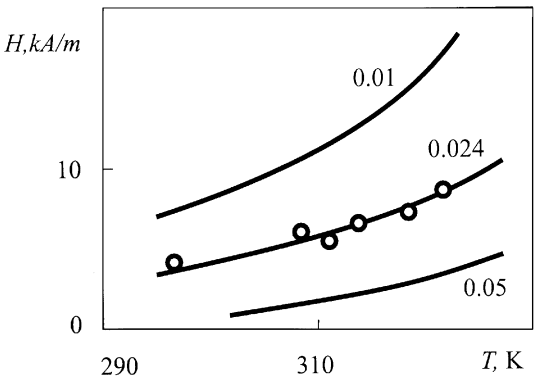

Fig. 1. Phase stability diagram: critical magnetic field versus temperature at various magnetic phase concentrations (numbers on the curves), dots – experimental data from A.F. Pshenichnikov et al. (private communication).

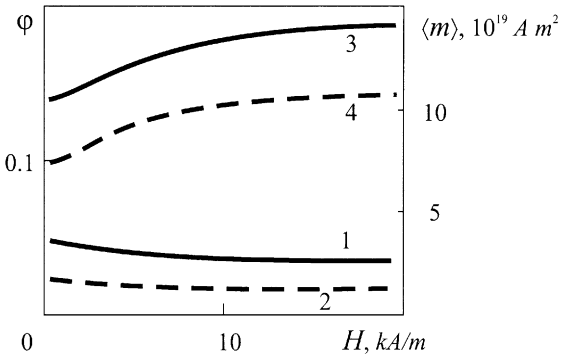

Fig. 2. Magnetic phase concentrations (solid) and mean magnetic moments (dashed) of the coexisting phases I (curves 1 and 3) and II (curves 2 and 4) for the model bidisperse MF as a function of an external field strength.

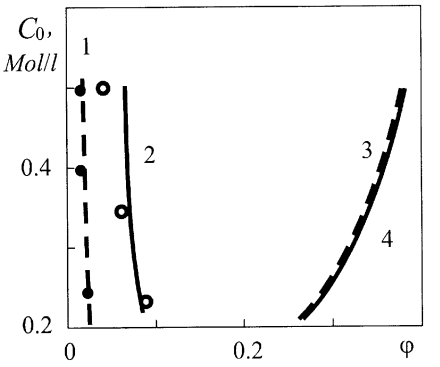

Fig. 3. Phase diagram of the bidisperse IFF at a volume particle concentration 2.5% (curves 1 and 3) and 8% (curves 2 and 4), dots – experimental data [2] for the IFF of the same concentrations.

several times larger than that in the original MF. Due to the high concentration and the large size of particles, the magnetic permeability of the substance in phase II is up to $\sim$ 30–40, which corresponds with well-known experimental results [1,8].

4. Phase separation in ionic ferrofluids

The ionic ferrofluids (IFF) are stabilized due to the formation of electrical double layers and the appearance of an interparticle repulsive energy barrier. The presence of an excess electrolyte in a carrier liquid leads to strong screening of the surface particle charge and to dramatic thinning of the electrical double layer. Thus, a sufficiently deep secondary energy minimum can appear due to the van der Waals and magneto-dipole interparticle attraction. With the presence of a high-energy barrier, which prevents irreversible coagulation, this minimum is to be capable for the IFF phase separation under the influence of an excess electrolyte [2,8].

The structure of the electrical double layers in the model bidisperse IFF may be determined in terms of Poisson–Boltzmann equation at the adsorbtion mechanism of the surface charge formation [7]. The ion adsorbtion results in the decrease of an electrolyte concentration in the solvent. This effect appears to be very strong: even in moderately concentrated IFFs with a ferroparticle volumetric content of about 10%, the real electrolyte concentration can be twice as low as the initial total concentration. Apparently, this is attributed to the presence of a large number of particles of first fraction with a highly developed specific surface area. As a result, the electrostatic repulsion in more concentrated IFFs becomes less screened. Characteristic plots for the interaction energy of the particles of fractions 1–1 and 1–2 exhibit a high potential barrier that prevents irreversible coagulation and virtually no secondary minimum. This means that the majority of ferroparticles of the 1st fraction behaves itself in the IFF as a thermodynamically stable weakly non-ideal gas. At the same time, the interaction energy of the particles of the 2nd fraction with each other is featured by a sufficiently deep secondary minimum, which can produce a condensation. Naturally, this refers only to the case of high electrolyte concentration.

A typical phase diagram of a bidisperse IFF in the plane "electrolyte concentration–ferroparticle concentration" is shown in Fig. 3. Curves on the left-hand and right-hand sides corresponds to concentrations of phases I and II, respectively. As expected, the phase diagram is dependent on the initial content of ferroparticles. To demonstrate this fact, two diagrams are presented in Fig. 3 for the IFF with the same fractional composition but with different ferrophase concentration. As is seen

from the figure, the left-hand branches of the phase diagrams are noticeably different. At the same time, the right-hand branches virtually coincide with each other. A similar behaviour of phase diagrams of real IFF was reported in [2,8].

5. Discussion

The basic results of the phase stability analysis are the following:

- the phase stability region is completely determined by the large particles, which allow for separation at room temperatures in weak-to-moderate magnetic fields and at very high ionic strength for ionic stabilized ferrofluids (Figs. 1 and 3);
- the strongly concentrated phase II (drop-like aggregates) contains very many large particles and very few small ones, whereas weakly concentrated phase I contains in the main only small particles;
- the drop-like aggregates occupy a small part of the volume of the system ($\leqslant 5\%$);
- the particle concentration in drop-like aggregates can be close to the one maximum possible for liquid state. Due to a high concentration and a large particle size (Fig. 2), initial susceptibility of droplet aggregates can be abnormally large: $4\pi\chi_L \sim 30$–40;
- the phase diagrams depend strongly on the concentration of initial bidisperse magnetic colloid (Figs. 1 and 3).

Acknowledgements

This work has been carried out with the financial support of the Russian Basic Research Foundation (Grant N 98-01-00031).

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